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# Relative Stability of the $^3A_2$ , $^1A_2$ , and $^1A_1$ States of Phenylnitrene: A Difference-Dedicated Configuration Interaction Calculation

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## ABSTRACT

The relative stability of the  $^3A_2$ ,  $^1A_2$ , and  $^1A_1$  states of phenylnitrene is evaluated by means of *ab initio* calculations followed by difference-dedicated configuration interaction (DDCI). This approach is based on effective Hamiltonian theory at a low order of perturbation to select rationally the determinants which contribute to the energy difference. The CI space built on this criterion is then treated variationally. The method allows a considerable reduction of the CI space compared with a complete CAS\*SDCI calculation (where CAS stands for complete active space). Depending on the concerned energy difference, different model spaces may be chosen, as illustrated in the  $^3A_2 \rightarrow ^1A_2$  and the  $^3A_2 \rightarrow ^1A_1$  transitions in phenylnitrene. Since the CI space may reach considerable dimensions, a direct CI algorithm for selected CI spaces, the SCIEL algorithm, has been used to perform the calculations. The results are in excellent agreement with previous calculations and with available experimental data. © 1996 by John Wiley & Sons, Inc.

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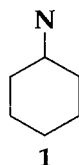
## Introduction

The reactive intermediate phenylnitrene PhN, **1**, is generated by thermolysis or photolysis of phenylazide. The initially generated  $^1A_2$  state of PhN undergoes intersystem crossing to yield the

triplet state  $^3A_2$ , which is known from an early electron paramagnetic resonance (EPR) determination<sup>1</sup> to be the ground state. However, regarding the magnitude of the triplet-singlet separation, some contradictory results have been reported that can be interpreted on the basis of the high reactivity of this intermediate. A first triplet-singlet splitting of 4.3 kcal mol<sup>-1</sup> was given by Drzaic and Brauman<sup>2</sup> from photodetachment spectroscopy experiments on the phenylnitrene anion. Although

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laser-induced fluorescence experiments on gas phase products of phenylazide photolysis performed by Ozawa et al.<sup>3</sup> seemed to confirm that the gap was small, in a later work the authors<sup>4</sup> interpreted the resulting spectrum through the rapid isomerization of phenylnitrene to cyanocyclopentadiene ( $C_5H_5CN$ ) and proposed a much higher separation based on *ab initio* calculations. In the last two years, new photodetachment experiments on the PhN anion<sup>5,6</sup> have given coincident values of 18 kcal mol<sup>-1</sup> for this splitting, and at the same time two theoretical works<sup>7,8</sup> have given support to this value. Both *ab initio* calculations have been performed with valence double  $\zeta$  plus polarization (DZP) basis sets and include correlation. The results of Kim et al.<sup>7</sup> have been obtained from a two-reference single- and double-excited configuration interaction (SDCI), while those of Hrovat et al.<sup>8</sup> partially include single and double excitations, from a (8/8) multiconfigurational SCF (MCSCF) calculation.



Recently, we have presented a general strategy for the calculation of transition energies<sup>9</sup> which has given good agreement with the available full configuration interaction (FCI) results, as  $CH_2$  (ref. 9a) or  $SiH_2$  (ref. 9b). The difference-dedicated configuration interaction (DDCI) method is based on the effective Hamiltonian approach at a low order of perturbation as a criterion to select rationally the determinants which contribute directly to the considered transition. The so-built configuration interaction space is then treated variationally. The method is a generalization of a precedent proposal specifically oriented to the determination of singlet-triplet separations in biradical problems,<sup>10-12</sup> extended later to more general magnetic systems involving  $n$  unpaired electrons in  $n$  orbitals.<sup>13,14</sup> The advantage of the DDCI scheme is that it makes a physically grounded selection of the determinants of the CAS\*SDCI, which reduces the size of the CI space from the fourth power of the dimension of the basis set to the third power. The goal of the present work is to show the applicability of the method to determine electronic transitions in systems of chemical interest, after the good behavior shown by the method in benchmark calculations.<sup>9</sup> The excitation energies for the first two singlet

states  $^1A_2$  and  $^1A_1$  of PhN furnish a good example. Furthermore, the transitions in this molecule give examples of different types of model spaces. A brief recall of the principles of selection of the CI is given in next. Since these specific CI spaces may reach considerable dimensions, direct CI methods are needed in many cases. Later we recall the grounds of the selected CI with an excitation labeling (SCIEL) algorithm. The results are reported in this article.

### Selection of the CI Space for the Evaluation of Transition Energies from the Quasi-Degenerate Perturbation Theory: The DDCI Approach

The calculation of transition energies presents an inherent problem in obtaining accurate values from the difference of the energies of the considered states, since often the uncertainty on each value may be of the same order of magnitude than the difference itself. Many proposals have been made to evaluate directly energy differences.<sup>15</sup> Among them, several specific CIs have been proposed based on intuitive physical grounds.<sup>15g-j</sup> Our method is based on a zeroth-order description of the phenomenon in terms of  $n$  electrons in  $m$  active orbitals (in many cases, two electrons in two active orbitals) defining a zeroth-order model space. The configurations which contribute to the energy differences at the second order of the expansion of the effective Hamiltonian built on the model space are added to the CI space, which is treated variationally. This procedure will now be briefly recalled for two electrons in two active orbitals systems.

#### THE GENERAL PROBLEM OF TWO ELECTRONS IN TWO ACTIVE ORBITALS

If we consider the particular case of two electrons in two active molecular orbitals (MO), labeled  $\varphi$  and  $\varphi^*$ , with  $S_z = 0$ , the complete active space (CAS) is defined by four determinants

$$\begin{aligned}\Phi_1 &= |\dots \bar{p}p \dots \bar{\varphi}\varphi|, & \Phi_2 &= |\dots \bar{p}p \dots \bar{\varphi}\varphi^*|, \\ \Phi_3 &= |\dots \bar{p}p \dots \bar{\varphi}\varphi^*|, & \Phi_4 &= |\dots \bar{p}p \dots \bar{\varphi}^*\varphi|\end{aligned}$$

generating four states, three singlets and a triplet, and by using the quasi-degenerate perturbation theory (QDPT), a  $4 \times 4$  effective Hamiltonian may be built on that model space,  $S$ . Up to second

order, the elements of this effective Hamiltonian may be written

$$\langle \Phi_I | H_{\text{eff}}^{(2)} | \Phi_J \rangle = \langle \Phi_I | H | \Phi_J \rangle + \sum_{\Phi_\alpha \notin S} \frac{\langle \Phi_I | H | \Phi_\alpha \rangle \langle \Phi_\alpha | H | \Phi_J \rangle}{E_J^0 - E_\alpha^0}$$

where  $\Phi_I, \Phi_J$  belong to  $S$ ,  $\Phi_\alpha$  are all the determinants of the outer space interacting with them, and  $E_J^0$  and  $E_\alpha^0$  are the eigenvalues of the zeroth-order Hamiltonian  $H^0$ :

$$H^0 = \sum_{\Phi_I \in S} E_I^0 | \Phi_I \rangle \langle \Phi_I | + \sum_{\Phi_\alpha \notin S} E_\alpha^0 | \Phi_\alpha \rangle \langle \Phi_\alpha |$$

When analyzing the outer space determinants which contribute to the second-order correction of the effective Hamiltonian, the determinants  $\Phi_\alpha$  which are obtained from a determinant of  $S$  by a double excitation of the type

$$\Phi_\alpha = D_{pq,ij}^+ \Phi_I, \quad \text{with } D_{pq,ij}^+ = a_i^+ a_j^+ a_q a_p$$

(where  $p$  and  $q$  label inactive doubly occupied orbitals and  $i$  and  $j$  inactive virtual orbitals) do not contribute to the extradiagonal elements of  $H_{\text{eff}}^{(2)}$

$$\langle D_{pq,ij}^+ \Phi_I | H | \Phi_J \rangle = 0, \quad \text{if } I \neq J$$

since  $D_{pq,ij}^+ \Phi_I$  differ from  $\Phi_J$  by at least three orbitals. Moreover, these determinants only cause a shift of the diagonal elements since

$$\frac{\langle \Phi_I | H | \Phi_\alpha \rangle \langle \Phi_\alpha | H | \Phi_J \rangle}{E_I^0 - E_\alpha^0} = \frac{\langle pq || ij \rangle^2}{\Delta_{pq \rightarrow ij}}$$

provided that  $E_I^0 - E_\alpha^0$  is independent of  $E_I^0$ , as is the case with the Møller-Plesset definition of  $H_0$ :

$$H_{\text{MP}}^0 = \sum_I \varepsilon_I a_I^+ a_I$$

In consequence, these determinants do not contribute to the difference between the roots of the effective Hamiltonian. Thus, at this level of theory, only the excitations including three labels of inactive orbitals are relevant.

To get the searched energy differences, one possibility is to solve the eigen equation:

$$H_{\text{eff}} \Psi = E \Psi$$

However, it is known that near degeneracies and convergence problems are unavoidable and cause the appearance of intruder states. An alternative

procedure which avoids these problems, as well as the arbitrariness of the choice of  $H^0$ , and allows the inclusion of higher-order effects is to use the preceding perturbative arguments to construct a configuration interaction space including the most important contributions to the energy differences, but to evaluate these differences variationally. This CI space is generated by including the CAS determinants and all single and double substitutions on it involving at least one active MO. The advantage of this procedure over the inclusion of all singles and doubles on the CAS is that this difference-dedicated CI (DDCI) space grows only as the cube of the MO set dimension. On the other hand, the DDCI space may split into two subspaces of different symmetry if the irreducible representations (IRs) of  $\varphi$  and  $\varphi^*$  are not the same, and thus the open-shell determinants of the CAS do not belong to the most symmetric representation.

The next step of the procedure consists of diagonalization of this space of single and double excitations to obtain the searched transitions as the difference between the concerned roots of the variational DDCI if both states belong to the same IR, or as the difference between the corresponding eigenvalues of the diagonalization of the subspaces belonging to each IR.

## THE PARTICULAR CASE OF BIRADICALAR SYSTEMS

Biradicalar systems are interesting cases of two electrons in two active MOs. In these systems,  $\varphi$  and  $\varphi^*$  are nearly degenerate, and it is useful to analyze the problem from a valence bond point of view. If we perform a unitary transformation of the active orbitals into localized MOs by a simple  $\pi/4$  rotation,

$$a, b = 2^{-1/2}(\varphi \pm \varphi^*)$$

it can be easily shown that the first singlet and the triplet state may be described in terms of the neutral VB forms:

$$\begin{aligned} {}^1\Psi &= 2^{-1/2} [ |\dots \bar{p}p \dots \bar{a}b| + |\dots \bar{p}p \dots \bar{b}a| ] \\ {}^3\Psi &= 2^{-1/2} [ |\dots \bar{p}p \dots \bar{a}b| - |\dots \bar{p}p \dots \bar{b}a| ] \end{aligned}$$

whereas the remaining two singlets have essentially ionic character:

$${}^1\Psi', {}^1\Psi'' = 2^{-1/2} [ |\dots \bar{p}p \dots \bar{a}a| \pm |\dots \bar{p}p \dots \bar{b}b| ]$$

Thus, for  $^1,^3\Psi$ , a  $2 \times 2$  effective Hamiltonian may be built on the model space generated by the two neutral forms. Since both generators differ by two spinorbitals, the part of the outer space contributing to the extradiagonal matrix element includes only the determinants  $|\Phi_\alpha\rangle$  with one or two inactive orbitals. Hence, the DDCI space is reduced to single and double substitutions with at least two active MOs in holes or particles (labeled DDCI2). Provided that all the determinants ensuring that the wave function is an eigenstate of  $S^2$  are included, the DDCI is invariant under the unitary transformation of the active orbitals, and it is possible to generate the differential space in the original symmetry group of the molecule. The advantage in this case is that the size of the space grows only as the square of the dimension of the MO set.

### CORRECTION FOR ADIABATIC TRANSITIONS

In the preceding considerations, we have supposed that the correlation energy of the inactive electron pairs was constant under the transition. But geometrical changes in the adiabatic transitions may be important and induce significant changes in the molecular orbitals; the contribution of the double excitations  $pq \rightarrow ij$  can no longer be considered constant. The simplest way of accounting for this contribution is to estimate it at the MP2 level

$$\sum_{p,q,i,j} \frac{\langle pq||ij\rangle^2}{\Delta_{pq \rightarrow ij}}$$

for each geometry, and to add its variation to the variational difference.

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### The SCIEL Direct CI Scheme

Although the growth of size of the DDCI space with the MO basis set is not as fast as for a complete CAS\*SDCI (since in the worst case it grows as the third instead of the fourth power of the dimension of the MO set), when large molecular basis sets are considered, it easily reaches some hundred thousand determinants. The disk requirements to store the nonzero matrix elements increase rapidly, and direct algorithms are suitable alternatives for the diagonalization of these CIs.

Direct CI algorithms applied to full CI (FCI) problems have been proposed and improved during the last decade.<sup>16</sup> On the other hand, two general algorithms allowing us to perform direct

selected CIs have recently been described, one based on the string formalism<sup>17</sup> and the other proposed by one of us and co-workers using the hole-particle formalism,<sup>18</sup> SCIEL (Selected CI with excitation labeling), suitable to treat the DDCI spaces described earlier, which are particular cases of selected spaces since they do not include all the possible single and double excitations on a reference space. We will give now the outlines of the SCIEL method.

In the hole-particle formalism, a given determinant is defined as the product of a multiple excitation concerning  $\alpha$  electrons by a multiple excitation concerning  $\beta$  electrons:

$$\Phi_I = I_\alpha I_\beta \Phi_0, \quad \Phi_I \in M$$

where  $\Phi_0$  is the reference ground state, taken as the vacuum state, and  $M$  is the selected CI space.

The multiple excitation  $I_\alpha$  ( $I_\beta$ ) may be expressed as a product of monoexcitations  $a_s^+ a_r$ , until the excitation degree in  $\alpha$  (or  $\beta$ ):

$$I_\alpha = \prod_m a_s^+(m) a_r(m)$$

The definition is unique provided that labels of holes and particles are ordered and each  $I_\alpha$  receives a lexical label. Since in a selected CI not all the possible  $I_\alpha$  are active, the active labels are contracted in an ordered list,  $L$ , so that the  $I_\alpha$  is characterized by its position in the list. When  $S_z = 0$ , the  $I_\alpha$  and  $I_\beta$  lists are identical and stored once. The determinant  $\Phi_I$  is identified by the positions of both  $I_\alpha$  and  $I_\beta$  labels, and the set of determinants is ordered in increasing  $I_\alpha$  labels and for each  $I_\alpha$  increasing  $I_\beta$  label coupled to it.

A direct CI procedure solves the matrix equation

$$Hc = Ec$$

without storing the Hamiltonian matrix elements. In the Davidson's procedure,<sup>19</sup> at the  $m + 1$  iteration the vector coefficients are obtained from

$$c_f^{m+1} = \frac{\sigma_f^m - E^m c_f^m}{E^m - H_{ff}} + c_f^m$$

where

$$\sigma_f^m = \sum_I H_{If} c_I^m, \quad H_{If} = \langle \Phi_f | H | \Phi_I \rangle$$

$$\text{and } E^m = \sum_f \sigma_f^m c_f^m$$

The action of the Hamiltonian operator may be partitioned into three types of operations:

1. One-electron processes  $a_s^+ a_r$ , which involve the operations  $F_{rs} a_s^+ a_r$ .
2. Bielectronic  $\alpha\beta$  operations  $\langle rt|su \rangle a_u^+ a_t a_s^+ a_r$ . Operations 1 and 2 are performed very rapidly since for each  $I_\alpha$  and each symmetry of the product  $rs$ , the operations  $a_s^+ a_r$  active on it to give an active  $J_\alpha$

$$J_\alpha = \pm a_s^+ a_r I_\alpha$$

are stored. The effective operations, their sign, and the label of  $J_\alpha$  are stored for each  $I_\alpha$ . An inner loop is performed for  $\beta$  operations, and finally if the determinant  $\Phi_j = J_\alpha J_\beta \Phi_0$  belongs to the CI space, the contribution is added to  $\sigma_j$ . The algorithm corresponding to  $\alpha\beta$  operations is shown in Scheme 1.

3. Bielectronic  $\alpha\alpha$  (or  $\beta\beta$ ) operations  $\langle rt||su \rangle a_u^+ a_t a_s^+ a_r$ . Since many of the intermediate mono-electronic operations  $a_s^+ a_r I_\alpha$  (or  $\beta$ ) in a selected CI do not belong to the list, these double substitutions are performed at each iteration, and if they give an active  $J_\alpha$  ( $J_\beta$ )

$$J_\alpha = \pm a_u^+ a_t a_s^+ a_r I_\alpha$$

the loop on unchanged coupled  $I_\beta$  ( $I_\alpha$ ) is performed. If the determinant  $\Phi_j = J_\alpha I_\beta \Phi_0$  belongs to the CI space, the contribution is added to the corresponding element of  $\sigma$ . This part of the algorithm is shown in Scheme 2.

```

Do  $I_\alpha \in L$ 
  Do  $a_s^+ a_r$  (active on  $I_\alpha$ )
     $J_\alpha = \text{sign}(rs) a_s^+ a_r I_\alpha$ 
    Do  $I_\beta$  (coupled to  $I_\alpha$ )
       $\Phi_i = I_\alpha I_\beta \Phi_0$ 
      Do  $a_u^+ a_t$  (active on  $I_\beta$ )
         $J_\beta = \text{sign}(tu) a_u^+ a_t I_\beta$ 
         $\Phi_j = J_\alpha J_\beta \Phi_0$ 
        If  $\Phi_j \in M$ ,  $\sigma_j = \sigma_j + \text{sign}(rs) \text{sign}(tu) \langle rt|su \rangle \cdot c_j$ 
      end
    end
  end
end

```

**SCHEME 1.** SCIEL. Bielectronic  $\alpha\beta$  operations.

```

Do  $I_\alpha \in L$  (excitation degree ni)
  Do  $a_u^+ a_t a_s^+ a_r$ 
     $J_\alpha = \text{sign}(rstu) a_u^+ a_t a_s^+ a_r I_\alpha$  (excitation degree nj  $\leq$  ni)
    If  $J_\alpha \in L$  then
      Do  $I_\beta$  (coupled to  $I_\alpha$ )
         $\Phi_j = J_\alpha I_\beta \Phi_0$ 
        If  $\Phi_j \in M$  then
           $\Phi_i = I_\alpha I_\beta \Phi_0$ 
           $\sigma_i = \sigma_i + \text{sign}(rstu) \langle rt||su \rangle \cdot c_j$ 
          If  $nj < ni$ ,  $\sigma_j = \sigma_j + \text{sign}(rstu) \langle rt||su \rangle \cdot c_j$ 
        end
      end
    end
  end
end

```

**SCHEME 2.** SCIEL algorithm. Bielectronic  $\alpha\alpha$  operations.

Similar schemes are also used for selected direct CI procedures in the string formalism.<sup>17</sup> The advantage of the hole-particle labeling, especially when only low excitation degrees are used, derives from the formal distinction between excitation and deexcitation processes, since the first depend on the square of the dimension of the occupied MO set multiplied by the dimension of the virtual MO set, and the second depend on the square of the excitation degree only. However, the symmetry of the coupling between determinants  $\Phi_i$  and  $\Phi_j$  may be used to add simultaneously the corresponding contributions to  $\sigma_i$  and  $\sigma_j$ , by sweeping only the deexcitation processes.

## Results

### COMPUTATIONAL DETAILS

*Ab initio* all-electron calculations have been performed with the 6-31G\* basis set on the three lowest states of phenylnitrene, the triplet  $^3A_2$  and the singlets  $^1A_2$  and  $^1A_1$ . The geometries given by Hrovat et al.<sup>8</sup> optimized with the 3-21G basis set at the (8/8) CASSCF level, have been taken. After the SCF step, the differential subspace is generated and diagonalized for each state. The transition energies are obtained by the difference between the eigenvalues corresponding to each state. The difference between the MP2 contribution of the inactive orbitals for each state is then added. The

1s orbitals of carbon and nitrogen have been frozen at the CI level.

### RELATIVE STABILITY OF THE $^3A_2$ , THE $^1A_2$ , AND THE $^1A_1$ STATES IN PHENYLNITRENE

Two different situations arise for the transitions  $^3A_2 \rightarrow ^1A_2$  and  $^3A_2 \rightarrow ^1A_1$ . Both open-shell states,  $^3,1A_2$ , correspond to the configuration  $\dots 1a_2^2 8b_2 3b_1$  and are described at the zeroth order with  $S_z = 0$  through the determinants  $\Phi_1 = |\dots 8b_2 3\bar{b}_1|$  and  $\Phi_2 = |\dots 3b_1 8\bar{b}_2|$ :

$$^{1,3}\Psi = 2^{-1/2}[\Phi_1 \pm \Phi_2]$$

Since at the zeroth order the model space is generated by  $\Phi_1$  and  $\Phi_2$ , in the  $2 \times 2$  effective Hamiltonian elements, the contributions to the triplet-singlet splitting are given by determinants of the outer space, including excitations with at least two active MO indexes. The size of the DDCI2 space of  $A_2$  symmetry is small, since it only involves 5056 determinants. The splitting is then obtained from the difference of the roots. The results are given in Table I. The variational separation is 23.0 kcal mol $^{-1}$ , but because of the geometry changes, the contribution at the MP2 level of the excitations involving only inactive MOs is important, of -4.1 kcal mol $^{-1}$ , and reduces the gap to 18.9 kcal mol $^{-1}$ . This result is in good agreement with the calculations performed with basis sets of the same quality followed by a correlation treatment at the SDCl level, including the Davidson's correction<sup>20</sup> of Kim

**TABLE I.**  
Adiabatic Separation between the Ground Triplet  $^3A_2$  and the Lowest Singlet  $^1A_2$  in PhenylNitrene, in kcal mol $^{-1}$ .

	This Work	CISD + Q <sup>a</sup>	$\sigma S, \pi$ SDCl <sup>b</sup>	Exp.
$\Delta E_{\text{DIF}}$	23.0			
$\Delta E_{\text{MP2}}$	-4.1			
$\Delta E_{\text{ST}}$	18.9	18.3	18.3	
$\Delta E_{\text{ST(ZPE)}}$	18.3	17.7		$18.3 \pm 0.7^c$ $18 \pm 2^d$

$\Delta E_{\text{DIF}}$ : Variational calculation with the differential CI space;  $\Delta E_{\text{MP2}}$ : MP2 evaluation of the contribution of the inactive orbitals;  $\Delta E_{\text{ST(ZPE)}}$ : triplet-singlet separation including the zero point energy correction.

<sup>a</sup>Ref. 7.

<sup>b</sup>Ref. 8.

<sup>c</sup>Ref. 6.

<sup>d</sup>Ref. 5.

et al.,<sup>7</sup> who report a gap of 18.3 kcal mol $^{-1}$  with a CI space including about 678,000 state configurations, as well as with those of Hrovat et al.,<sup>8</sup> in which the CI space is restricted to  $\sigma$ -S,  $\pi$ -SD. When corrected by the zero point vibrational energy, the gap is in excellent agreement with the experimental values.

The electronic configuration for the  $^1A_1$  singlet is  $\dots 1a_2^2 8b_2^2$ , and at the zeroth order it is described by the linear combination of the closed-shell determinants  $\Phi_3 = |\dots 8b_2^2|$  and  $\Phi_4 = |\dots 3b_1^2|$ :

$$^1\Psi' = \lambda\Phi_3 - \mu\Phi_4$$

The model space that allows us to treat the triplet and this singlet is generated now by four determinants, and the outer space contributions to the extradiagonal elements of the  $4 \times 4$  effective Hamiltonian are given by excitations with up to three inactive MOs. Since each state belongs to different irreducible representations, the DDCI splits in two spaces, one of  $A_1$  symmetry with 201,307 determinants, the other of  $A_2$  symmetry with 200,954 determinants. The first root for each symmetry has been obtained with the SCIEL program. The results are shown in Table II. The variational separation of 33.3 kcal mol $^{-1}$  is reduced by 2.5 kcal mol $^{-1}$  when the MP2 correction is added. The zero point energy correction leads to a separation of 30.6 kcal mol $^{-1}$ , in agreement with that of Kim et al.,<sup>7</sup> 32.3 kcal mol $^{-1}$ , and lower than the value given by Hrovat et al.,<sup>8</sup> 38.7 kcal mol $^{-1}$ . The better agreement with the first result is reasonable, since the DDCI space includes all the single and double excitations from the double-configuration reference space which contribute at the second order of perturbation to the energy difference. The size of the CI calculation is, however, significantly

**TABLE II.**  
Adiabatic Energy Difference between the Triplet  $^3A_2$  and the Singlet  $^1A_1$  in PhenylNitrene, in kcal mol $^{-1}$ .

	This Work	CISD + Q <sup>a</sup>	$\sigma S, \pi$ SDCl <sup>b</sup>
$\Delta E_{\text{DIF}}$	33.3		
$\Delta E_{\text{MP2}}$	-2.5		
$\Delta E_{\text{ST}}$	30.8	32.3	38.7
$\Delta E_{\text{ST(ZPE)}}$	30.6		

$\Delta E_{\text{DIF}}$ : Variational calculation with the differential CI space;  $\Delta E_{\text{MP2}}$ : MP2 evaluation of the contribution of the inactive orbitals;  $\Delta E_{\text{ST(ZPE)}}$ : triplet-singlet separation including the zero point energy correction.

<sup>a</sup>Ref. 7.

<sup>b</sup>Ref. 8.

reduced. To our knowledge, no experimental value has been reported for this excitation energy.

## Conclusion

The present work shows that the procedure to evaluate variationally energy transitions based on specific CIs selected from the choice of a minimal model space and a low perturbative development of the corresponding effective Hamiltonian provides results which are in good agreement with experience and with those obtained by larger-size CI. The reduction of the CI space is particularly important when biradicals are involved, as in the  $^3A_2 \rightarrow ^1A_2$  transition in PhN.

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